

Syngas Chemical Looping: Particle Production Scale Up and Kinetics Investigation

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Abstract

The syngas chemical looping process (SCL) is a novel method for the conversion of carbonaceous fuels to both electricity and hydrogen while capturing carbon dioxide and other pollutants. Since coal is a pollutant intensive carbon based fuel, conventional coal based energy conversion systems with inadequate pollutant control devices have been criticized for emissions of CO₂ and various other pollutants. The SCL process has the potential to transform the conventional coal conversion processes to a clean, zero emissions process. The separation of CO₂ and other contaminants is inherent in SCL, hence no dedicated pollutant control device is required. At the heart of the SCL process is an oxygen carrying metal oxide particle. The scale up of particle production was investigated because the total throughput of the process is directly proportional to the amount of particles being recycled. At present, particles are synthesized through pelletization of composite powders. The production rate of the particles was limited since the fine composite powders (2 – 7 microns) were constantly clogging during the feeding step. Through size increase of the composite powders to 425 – 1000 microns via granulation, clogging was significantly reduced. In addition to scale up of the particles, kinetic studies on particle size were also carried out. Results show that particle size is not a significant factor in the determination of the reaction rate. Pressure effects on the oxygen carrier reaction kinetics were also investigated. A high pressure thermogravimetric analyzer was used to study pressure effects by measuring mass changes of the oxygen carrier with time. A previous study stating that iron reactivity decreased with pressure was disproved. Pressure effects were investigated by maintaining the same molar flow rate and mole fraction of hydrogen with the balance of

nitrogen. The reaction kinetics increased with pressure and temperature over the pressure range of 1.3 atm to 30 atm and temperatures between 700 to 800 °C. There was also evidence of the presence of a boundary layer at higher pressures which caused a mass transfer limitation with regard to reaction rate. The previous claim was found to be attributed to the formation of the reactant gas boundary layer around the particles.

To my family and friends whom I love.

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I would like to thank Dr. L.-S. Fan for providing the opportunity to perform undergraduate research with his group. Through research, I have learned much regarding clean coal technology, how to apply my knowledge to practical problems, and more about myself. Without the opportunities that Dr. Fan has provided me, I would not be the same person that I am today.

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My family has always been supportive of my goals in education even when I had been unsure of them myself. They have worked hard to support my studies, and I owe much of what I have accomplished to them because I have made their work ethic my own. Without them, I would not be here today.

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Introduction

Environment and Energy

Since the Industrial Revolution in the 1700's, the use of fossil fuels and deforestation has increased the atmospheric carbon dioxide levels in the atmosphere. In 2005, the atmospheric concentration of carbon dioxide was 35% higher than the level before the Industrial Revolution according to the Environmental Protection Agency¹. Carbon dioxide is a greenhouse gas which absorbs and emits radiation back onto the earth. This reemission has caused the average temperature of the earth to increase by 1.0 to 1.7 degrees Fahrenheit². Figure 1 given below shows the major greenhouse gases responsible for the temperature rise, and carbon dioxide is responsible for more than half of the radiation emitted back to the Earth's surface.

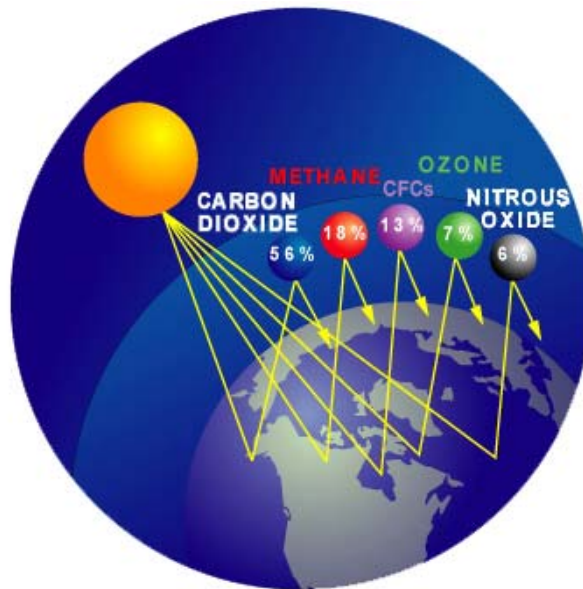


Figure 1: Greenhouse gases and energy emissions³

This change in temperature causes expansion of ocean water and widespread melting of snow and ice which leads to rising sea levels. Rising sea levels will have many adverse effects on weather conditions and geographical conditions. These effects

include loss of wetlands and increased salinity in rivers to increased flooding. Because of the potential for damage due to global warming caused by an imbalance in greenhouse gases, much emphasis has been put into motion to slow or stop the carbon dioxide emissions from human processes.

The world demand for energy increases and will continue to increase. According to the World Energy Outlook published by USDOE ⁴, the demand for energy derived from fossil fuels will continue to increase until the year 2030. Oil will have the largest share of the fossil energy, and coal is the second largest share. Coal based energy will have the largest increase in demand specifically for electric power generation. As the demand for oil increases, the dependence on foreign oil also increases. Middle Eastern countries possess approximately 56% of the world's oil reserves and 34% of the natural gas reserves. The Middle East is subject to political turmoil and violent uprisings which threaten to disrupt the supply of oil. Due to oil dependence, a disruption in the supply of oil would then have severe repercussions on both economic and technological growth. On the other side of the fossil fuel coin, the majority of the world's coal reserves reside in the United States, Europe, Russian, India, and China. Due to abundance in coal reserves and the depleting supply of the world's oil, coal is expected to be a major player in the future of meeting world's energy requirements.

While liquid fuels are still expected to be the most dominant player in 2030 for energy consumption in general, coal is the dominant player in electricity production. The usage of coal is expected to increase the most rapidly in terms of electricity production. Part of the reason for the sharp increase is due to China as they alone count for 71 percent of the increase due to their desire for economic growth. Figure 2 given below shows the

world's energy use by fuel type. As can be seen, liquid fuels are expected to remain dominant with coal derived energy increasing at a faster rate than the others. Figure 3 shows a similar trend for coal except the data shows fuels used for electricity generation.

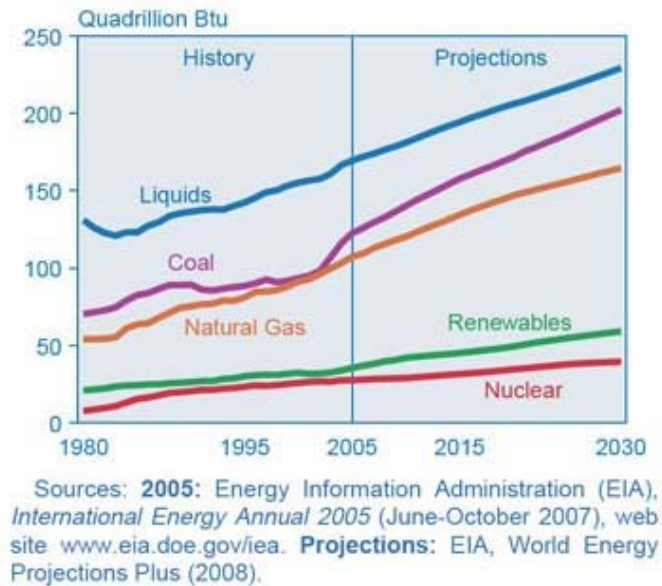


Figure 2: Energy use by fuel type⁵

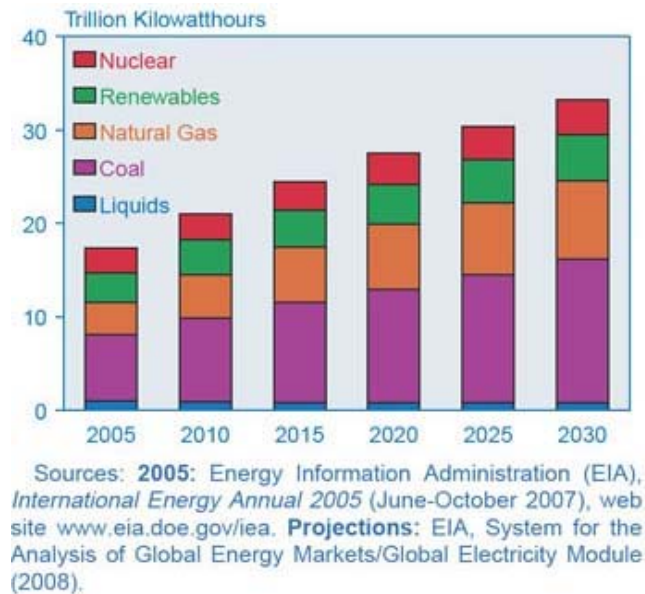


Figure 3: Electricity use by fuel type

Since coal usage is expected to increase faster than other fuel types in order to satisfy the world's energy demands, it is important to find cleaner and more efficient ways to convert coal into electricity, hydrogen, or other suitable energy carriers.

According to the Department of Energy, hydrogen has the potential to both decrease the dependence on foreign oil and cut greenhouse gas emissions. Hydrogen is not an energy source because it cannot be found in nature as elemental gaseous hydrogen. Like electricity, hydrogen is an energy carrier. Hydrogen has the potential to decrease the dependencies on imported oil because it can be produced from sources such as coal or biomass. Moreover, hydrogen is capable of being produced from water using solar energy, which is carbon free. Hydrogen allows other energy sources to be converted to hydrogen for use which gives flexibility in the energy source and can help cut greenhouse gas emissions by allowing for a transition from fossil fuels to renewables.

Syngas Chemical Looping Process

The syngas chemical looping process (SCL) is centered on the use of an oxygen carrying metal oxide particle. The metal oxide is reduced and oxidized in a cyclic manner through the shuttling of oxygen. The entire process works by generating a syngas from either coal or another carbon based fuel through gasification. The syngas goes through some preliminary treatments for sulfur treatment. The treated syngas is then taken to the reducer where the metal oxide particle is reduced by transferring oxygen to the gas. The products of the reaction are mainly carbon dioxide, water, and the reduced iron particles which consist of Fe and FeO. The reduced metal oxide particles are then sent to the oxidizer where it reacts with steam. The steam reduces to hydrogen and causes the iron to oxidize up to Fe_3O_4 . The Fe_3O_4 particles are transferred to the

oxidizer with compressed air through the combustor. The combustor oxidizes the Fe_3O_4 back to Fe_2O_3 which completes the redox cycle. Figure 4 below shows the overall SCL process.

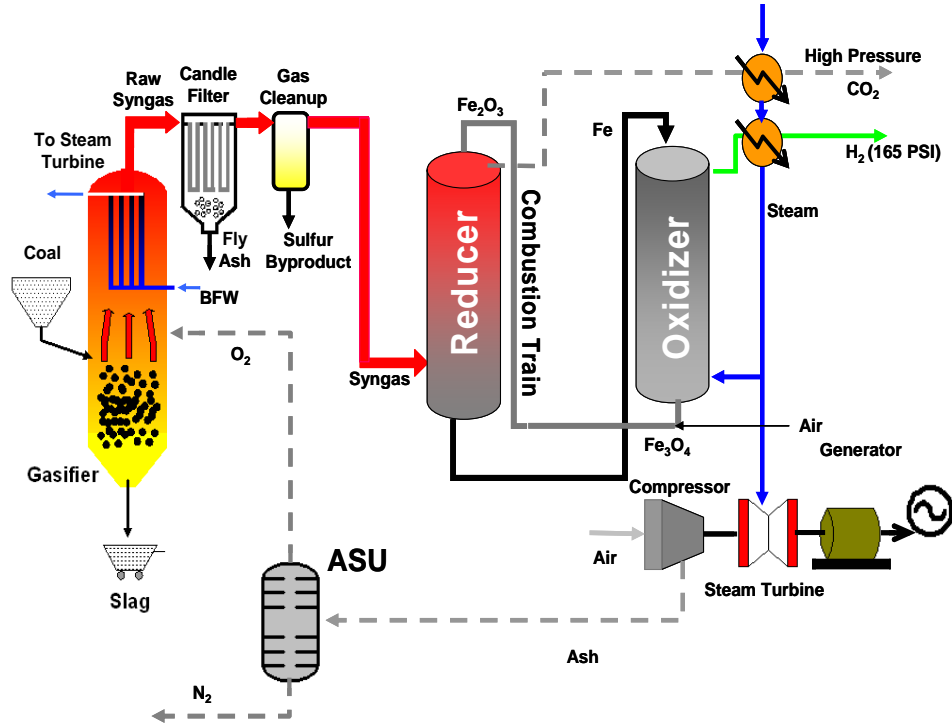
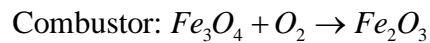
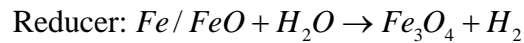
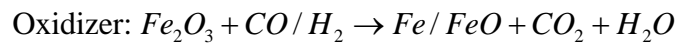


Figure 4: Syngas chemical looping process⁶

As can be seen above in Figure 4, the combustion of syngas and the hydrogen generation reaction occur in different reactors. Because of the different reactors in which the two steps occur, the separation of CO_2 is inherent in the process which means no additional separation steps are required. The key reactions for each reactor are given in Equation 1.



Equation 1: Key reactions of SCL reactors

This reduces the cost and complexity of the operation when compared to the traditional coal fired power plant if CO₂ separation is desired. With the inherent CO₂ separation, sequestration is economically feasible. One of the growing concerns over coal utilization is the release of CO₂ into the atmosphere. By sequestering CO₂, the overall process is carbon neutral meaning that there is no net amount of carbon released into the atmosphere.

The technology behind SCL makes it a possible transition to future energy conversion systems. Since there is potential for zero emissions for carbon dioxide and other pollutants, the SCL process is a clean coal process. Coal derived energy has recently been the target of environmental criticism due to the heavy CO₂, sulfur, and mercury emissions. Previously, clean coal had been economically prohibitive due to high parasitic energy requirements, but with this technology, clean coal is feasible. Moreover, because the oxygen carrier particle reacts with syngas and other carbonaceous fuel, it is not limited to coal. SCL technology can be applied to many carbonaceous feeds making it a robust and versatile process. SCL can be used with biofuels which would transform it into an alternative energy process. In the case that SCL is applied to biomass with carbon sequestration, it actually becomes carbon negative meaning that the process will have a net removal of carbon from the atmosphere.

In addition to being a carbon neutral process, SCL has the ability to not just produce electricity, but it has the capability of electricity and hydrogen cogeneration or it can be tailored to produce solely hydrogen. The hydrogen generated is 99.97%⁷ pure which is suitable for many applications, such as the Fischer-Tropsch synthesis, without further processing. Polymer fuel cell use however, requires hydrogen with sulfur

impurities at the ppb level. Further processing would be required; however since the process starts with a higher purity feed, operating costs are reduced.

Particles

Because the majority of the chemistry occurs within the reducer/oxidizer/combustion train cycle, the focus of this research was on the oxygen-carrier particles which are cycled between the three reactors. The gasifier could be approximated by using gas mixtures to represent syngas, but this study investigated the use of hydrogen and CO separately for the reduction of Fe_2O_3 .

The process itself has potential to be a green process due to the potential for carbon sequestration and the possibility of hydrogen and electricity cogeneration. The particles play an important role in how environmentally friendly the process can be. Due to the ability for the process to use other metal oxides, such as nickel, for the redox cycle, the particle composition can be chosen to also be environmentally friendly. Ni^{+2} is a known carcinogen and is a common chemical for use in the energy industry. It is used for catalytic purposes and possesses many of the desired qualities of an oxygen carrier, however, iron has been chosen over nickel because it is non-toxic, and in fact, the Fe^{+2} ion is important for normal human body function. Moreover, nickel is only suitable for heat generation whereas iron can also be used to produce hydrogen. Since iron is non-toxic, there are no adverse environmental effects in releasing iron oxides. More importantly for the process itself, iron has a high oxygen capacity which is the function of the metal oxide – to serve as an oxygen carrier. Iron has a +3 oxidation state while nickel has +2. With similar atomic weight, iron has a larger oxygen capacity.

An additional requirement for the properties of the iron pellets is recyclability.

The iron particles need to maintain reactivity over numerous redox cycles; however, raw iron powder does not provide the recyclability necessary. The recyclability can be increased with the addition of a ceramic support. The iron particles in this study are composed of 70% by mass iron(III) oxide and the balance of a support. In addition to improving recyclability due to reactivity, the support also provides some attrition resistance as the pellets will constantly be moving and have contact with other pellets in the SCL process. The last processing step which is mainly used for increasing the durability of the pellet is the sintering step. Though sintering, the grains of the iron will agglomerate with each other and the binder, thus making a stronger and more attrition resistant particle.

Alternatives Economy

The abilities of the SCL process places it in a unique position in relation to other processes. Because of the ability for hydrogen production and the feed flexibility the SCL process can serve to accelerate the transition from a fossil based economy to the alternative fuel economy. Its products can be used directly as fuels or be used as reagents in other processes. In the case of the Fischer-Tropsch process, it is generally applied in a coal or natural gas to liquids process, but in the case the hydrogen feedstock is generated from biomass, it can be considered a biomass to liquids process. By coupling this process with other technologies, SCL can use coal to make liquid fuels today, or it can use alternative energies to make hydrogen tomorrow. The SCL process is one with longevity, and it is poised to facilitate the transition to an alternative energy economy.

Experimental setup and procedure

Pelletization

Previously during pelletization, the pellets were created through the use of raw iron oxide and support powders. The pelletization procedure involves two main steps. The first step involved is the powder agglomeration which processes the raw powders into a composite powder, and the second step is the actual pelletization of the powder. The powder agglomeration is performed by dry mixing 70 wt% Fe_2O_3 powder and the balance of the support. Approximately 3 lbs of 1/2" diameter carbon steel media are placed into a rotary drum mixer, shown in Figure 5, along with the powders to promote mixing and gentle attrition of the chunks of raw powder. A solution of white corn starch is also prepared which would give the mixture before sintering a composition of 2 wt% starch to serve as an organic binder. While the Fe_2O_3 and the support are mixing, the starch solution is sprayed into the rotary drum mixer. This process is continued until the starch solution is spent. After mixing is complete, the powder will have agglomerated into a wide range of sizes ranging from the desired particle size under 1 mm to sizes up to 1 cm in diameter. The powder along with the steel media is dried in a small oven at 300 °F overnight. A picture of an oven used for the process is given below in Figure 6.



Figure 5: Drum mixer



Figure 6: Small drying oven

After drying, a system of sieve trays and an autosieve machine is used to grind and collect particles of the appropriate sizes. The autosieve operates by shaking sieves in the lateral direction with an arm which taps the top of the sieve stack. The carbon steel media will act as grinding media with the lateral movement. An image of the autosieve and grinding media are given below in Figure 7. The steel media promote attrition of the agglomerated iron oxide particles. As soon as the iron oxide particles fall below the screen spacing of the sieve, they fall to the next sieve where the process repeats itself. The process repeats until the desired particle size is achieved.

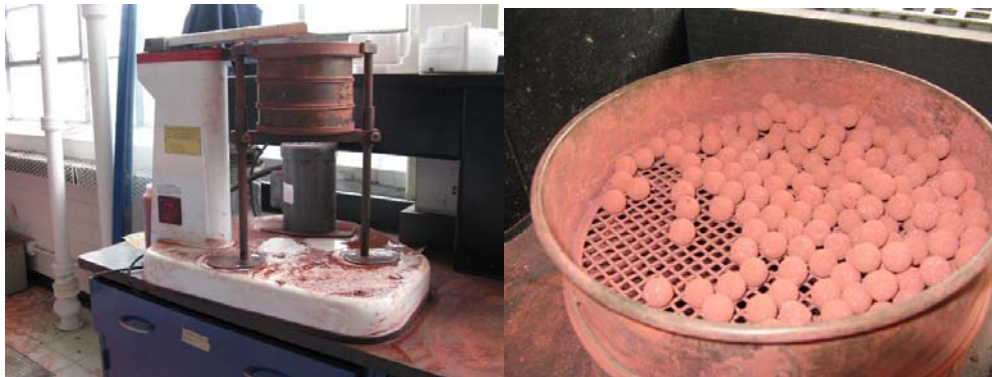


Figure 7: Autosieve and grinding media

The entire sieving process for a 2 kg batch of particles requires approximately 3 minutes to complete and cleans the media for the next batch of raw powder. The collected

powder is ready to be fed to the pelletizer or to be reprocessed in the rotary drum if the particle size is not within specifications. Two different pelletizers were used over the course of the study. One was used for smaller scale production and another was used in the scale up of the pelletizing process. The smaller pelletizer had stricter requirements as the powder size due to the tendency to clog. The larger pelletizer has less of a tendency to clog, but clogging is still a concern. The large pelletizer has a hopper which stores the powder and feeds into a rotary die set. The rotary die has a matching punch set which presses the powder into a pellet. Once the pellets are made, they are sintered in air at 900 °C overnight. The sintering process also causes the starch binder to burn off leaving only the iron oxide and the support.

Quartz High Temperatures Studies

The purpose of the quartz reactor studies was to study the effect of particle size, temperature, and partial pressure on reaction rate. The quartz reactor studies involved a furnace encasing a quartz tube which held a sample of particles. Within the quartz tube was a piece of quartz wool which suspended the particles while allowing reactant gasses to pass over the samples. A diagram of this is given in below in Figure 8. A photo of the reactor is given below in Figure 9.

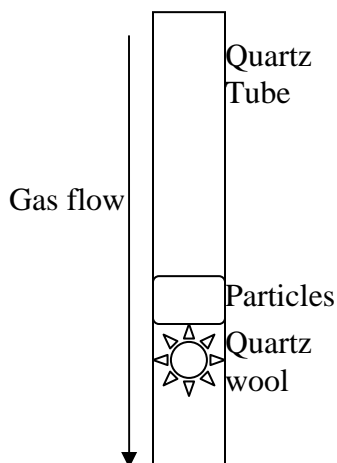


Figure 8: Quartz reactor diagram



Figure 9: Quartz reactor

The quartz reactor was used to reduce the composite iron particles. Particles of various sizes were reduced using carbon monoxide or hydrogen with the balance of nitrogen. The total flow rate was 2 Lmin^{-1} into a quartz tube with an inner diameter of $\frac{1}{4}$ ". The sample used was approximately 100 mg. The flow rate necessary to minimize the effect of a boundary layer was determined by measuring particle conversion with respect to time at different flow rates. When the conversion with respect to time no longer changed

as the flow rate increased, the critical flow rate was achieved. Using this method, the flow rate of 2 Lmin^{-1} was determined to be adequate. The flow of reactant gases were above the critical flow such that boundary layer effect was minimized.

Effect of Pressure on Reduction Rates

A high pressure ThermoGravimetric Analyzer (TGA) was used to measure the effects of temperature and pressure on the reduction kinetics of the composite particle. The TGA itself is capable of reaching temperatures up to 900°C and pressures up to 30 atm. The temperatures studied ranged from 700 to 900°C , and the pressures studied ranged from 1.3 to 30 atm. The TGA has several mass flow controllers for nitrogen and hydrogen control. A quartz sample holder was used to hold the samples during the experiments. The TGA itself has a stainless steel tube with approximately a 15 mm inner diameter which encases the reactant gasses and is water cooled to protect the balance. The furnace wraps around the stainless steel tube to provide heating to the sample and reactant gases. Computer control is used to control the furnace and the gas flows. The program used for both gas flow and temperature control is Pyris. Figure 10 shows the setup of the TGA.



Figure 10: High pressure thermogravimetric analyzer

In the operation of the TGA, the nitrogen was allowed to flow during the warm up period. After the appropriate temperature and pressure had been reached, the hydrogen was switched on to allow the reduction to occur. Approximately 0.12 g of particles were reduced by flowing a total flow rate of 420 mLmin^{-1} at STP (25°C and 1 atm) with 20 mol% hydrogen and the balance of nitrogen. A table with the pressure and temperature parameters is given below.

Experimental Design						
	Pressure (atm)					
Temperature (C)	1.3	2	5	10	20	30
700	x	x		x	x	
750	x			x	x	
800	x	x	x	x	x	x
850						
900	x					

Table 1: Experimental design

Results and Discussion

Pelletization

Previously, particle production was executed similarly to the process described in the experimental setup. The main difference was however, there was no particle agglomeration step. The change in particle size is proved to be an important parameter in particle production. By feeding the raw mixed powders, which have particle sizes of 3-5 microns, to the pelletizer the feeder would consistently become clogged within 5 minutes. It was determined that the clogging was due to the small particle size.

In order to verify that the small particle size was the major factor, the raw powder was agglomerated into larger particles through spraying with a water and starch solution⁸. After spraying and drying in the oven, the particles were forced by hand through sieves of various sizes, and specific ranges of particle sizes were collected. The clogging was found to be inversely related to particle size. The smallest particle size range consisting of particles smaller than 425 microns had the same problem as the raw powder. The second set of particles were within the size range of 425 – 710 microns and were found to be able to flow for longer periods of time. The second set was able to flow for approximately 10 – 20 minutes before becoming clogged and requiring attention. The largest particle size tested was 710 – 1000 microns. The largest particle size was able to be operated in the small pelletizer for approximately 30 minutes before clogging. The clogging was still due to the packing of the smaller particles as the vibrating nature of the feeder would cause particles to degrade into smaller pieces. The pelletizing process was moved to a larger pelletizer in order to increase production rate.

The large pelletizer is more robust in terms of particle size due to the larger feeding nozzle. Particle sizes smaller than 425 microns are able to be pelletized for longer periods of time than in the smaller pelletizer; however, there are still clogging issues. When the particle size includes all sizes under 1000 microns, the pelletizer is able to operate until the hopper is spent. By changing the particle size of the composite powder, the pelletization process has become much less labor intensive and the throughput has increased from the order of gday^{-1} to 20 kghr^{-1} .

Quartz High Temperature Reactor

The data from the quartz reactor showed that for particles within the size ranges of 125 – 250, 425 – 500, and 850 – 1000 microns, there was little difference in conversion time when reacted with carbon monoxide as shown in Figure 11.

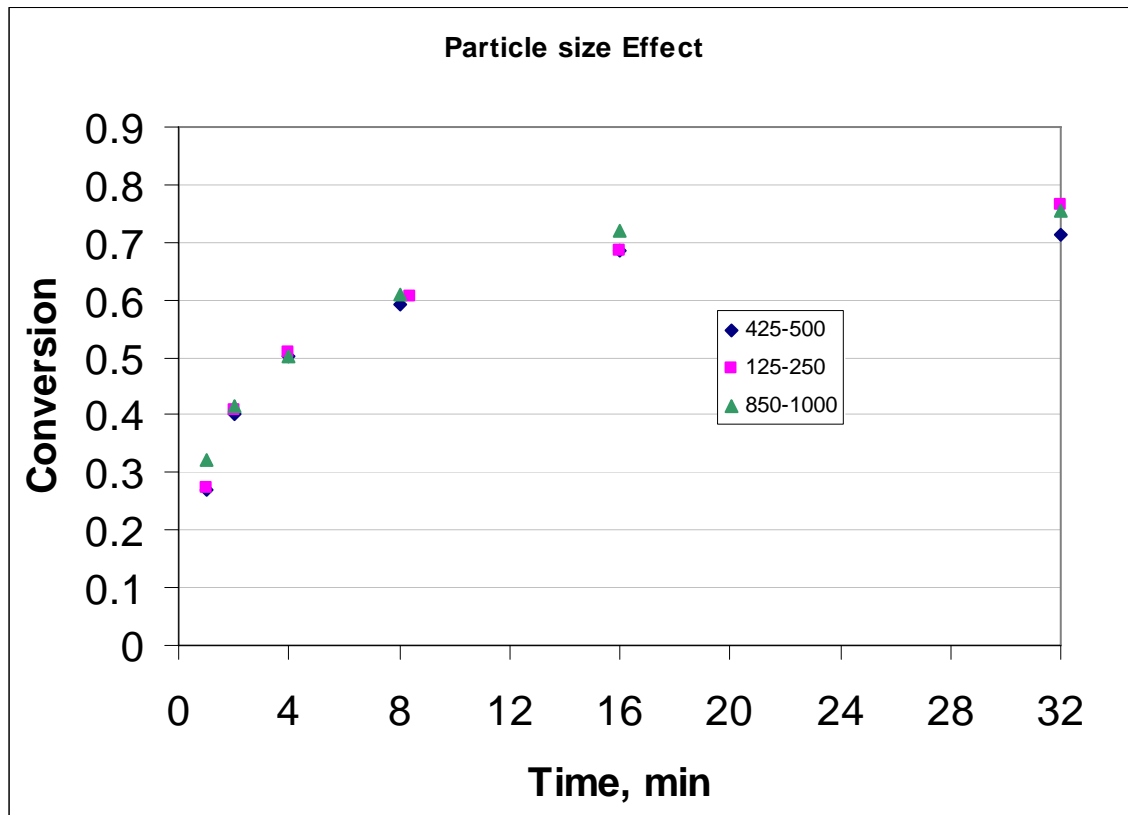


Figure 11: Particle size effect cycle 1

The experiment shown in Figure 11 was replicated except for the particle size group of 125 – 250 microns was replaced with a particle size range of 600 – 710 microns and the reactant gas was changed from carbon monoxide to hydrogen. As Figure 12 below shows, the results were replicated thus proving that particle size has little effect on reaction kinetics.

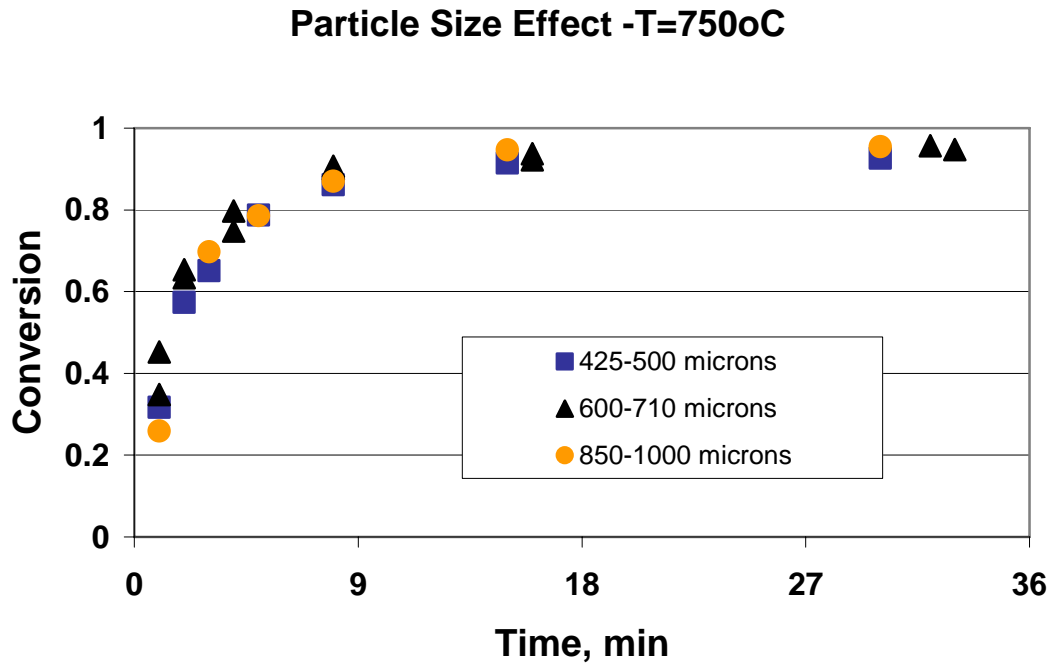


Figure 12: Particle size effect cycle 2

A study of reaction rate with respect to concentration was also conducted as shown in Figure 13. Gaseous concentrations can be viewed in different ways. One possible interpretation of changing gas concentrations is an increasing partial pressure. As the concentration of carbon monoxide increases, the partial pressure also increases accordingly. Figure 13 shows that the reaction rate increases with an increasing reactant concentration, or that the reaction rate increases with increasing partial pressure.

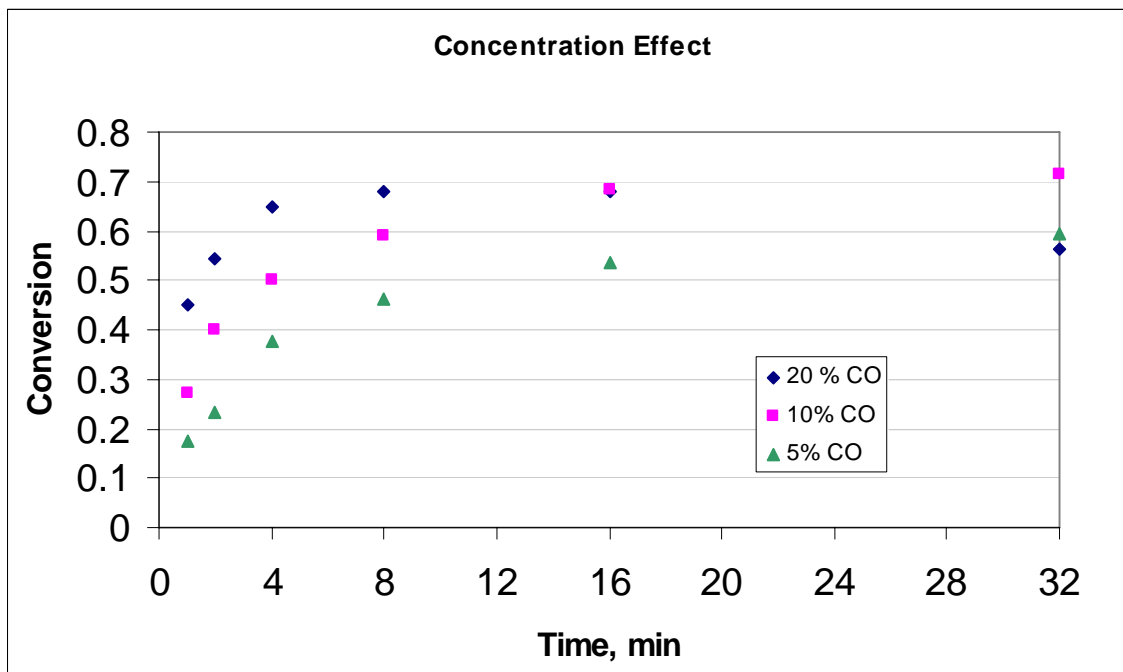


Figure 13: Concentration effect of CO on kinetics

Effect of Pressure on Reduction Rates

A previous kinetic study claimed that higher pressures lead to lower particle reactivities⁹, which contradicts to the observation in the quartz reactor, i.e. higher partial pressure leads to faster reaction rate. The data in support of the previous claim is given below in Figure 14. This result is in conflict with previously reported literature results¹⁰ which state that higher pressures lead to faster oxidation. The results for reductions were not given.

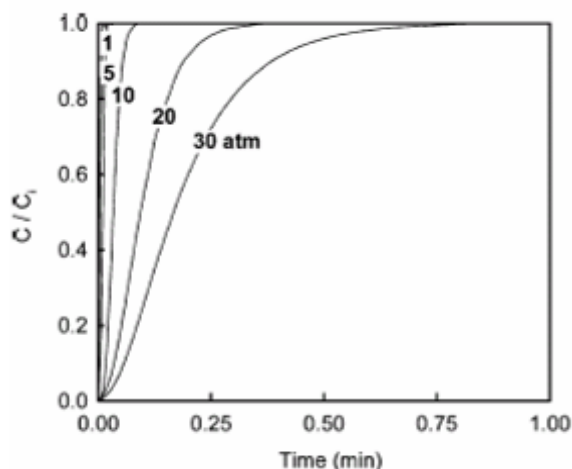


Figure 14: Kinetic data from previous study

In order to study the kinetics, data was taken mostly at 1.3 atm, 10 atm, and 20 atm with temperatures at 700 °C, 750 °C, and 800 °C. The original design included temperatures up to 900 °C and pressures up to 30 atm; however, due to unexpected problems with the hardware during experimentation, not all of the data at those pressures and temperatures were attainable. An additional problem encountered was that the data from the high pressure TGA suggested that the iron particles did not fully reduce. To prove that the iron particles did fully reduce, they were then oxidized in an atmospheric TGA using air. The results consistently showed that there was the expected ~27% mass increase for particles reduced at various pressures. The oxidation data from one sample reduced at 10 atm is given below in Figure 15, and the graph shows a 27% mass increase meaning that the sample had been fully reduced.

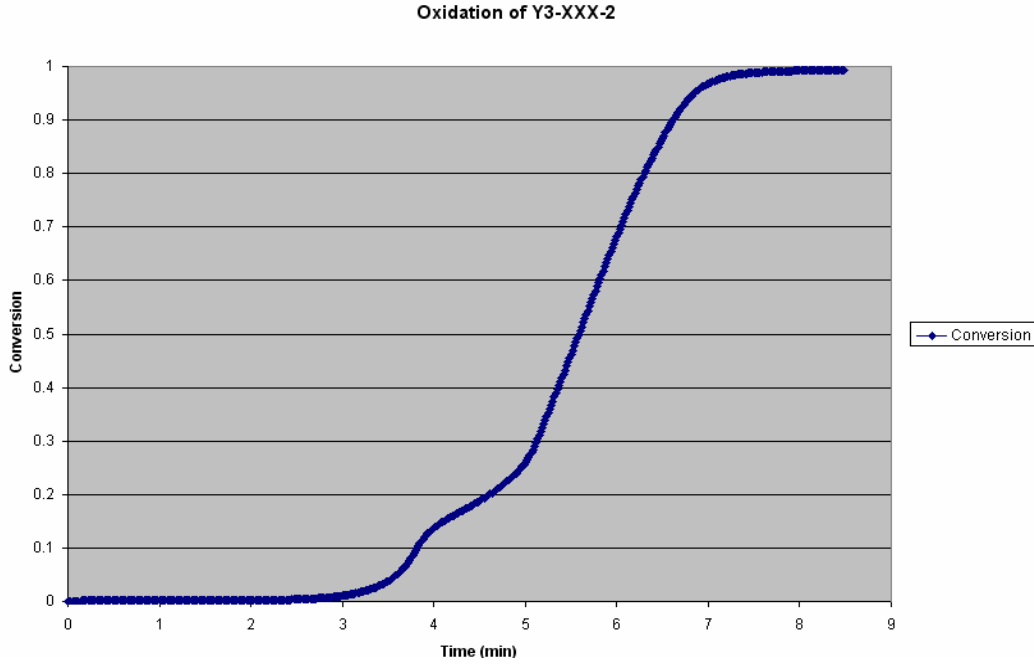


Figure 15: Verification of complete reduction through oxidation

The data for all pressures were then linearly scaled so that the experiments ended with a 21% mass decrease. The equation used to calculate the percentage mass change is given below in Equation 2 where M_{initial} is the weight just before turning on the hydrogen flow and M_{original} is the mass before heating. The percentage changes were then scaled to a final change of 21%. The data presented here, however, is scaled to 100% conversion.

$$\%change = \frac{M_{\text{current}} - M_{\text{initial}}}{M_{\text{original}}}$$

Equation 2: Percent mass change calculation

The kinetic data at low pressures show clear trends that the reactivity of the particle increases with temperature as shown in Figure 16. The data shown for temperatures 750 °C, 800 °C, and 900 °C clearly show a faster mass loss as temperature increases which is in agreement with kinetic theory. The time required to reach 50% conversion for 750 °C, 800 °C, and 900 °C are 6 min, 5 min, and 3 min respectively. The

50% conversion time is important because in the SCL process, the iron oxide is reduced to 50% of the original oxygen capacity before moving into the oxidizer.

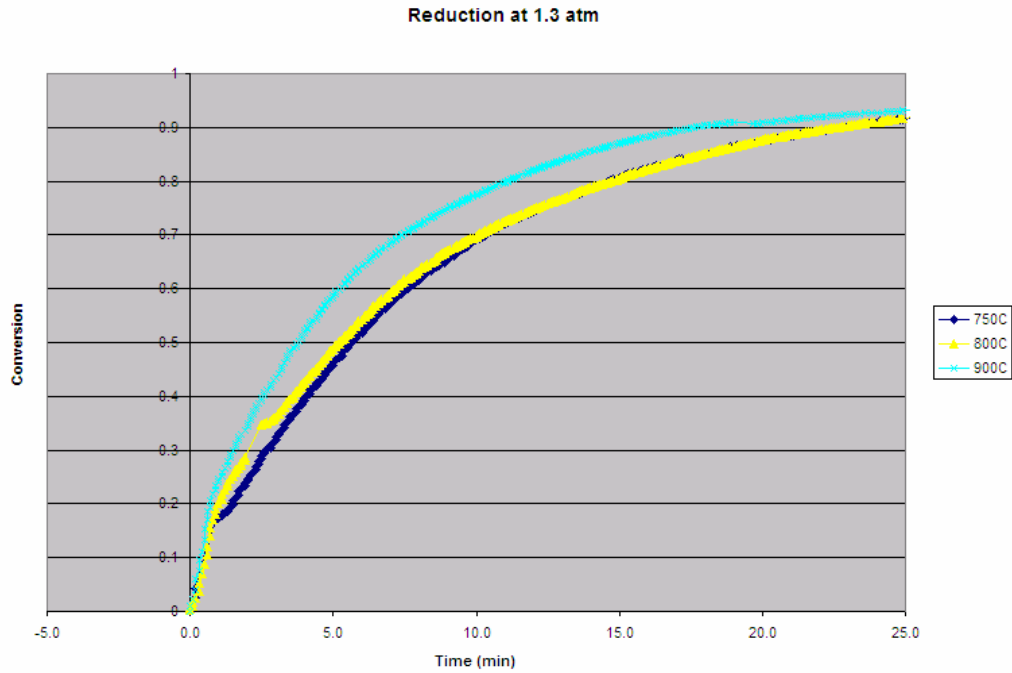


Figure 16: Reduction with hydrogen at 1.3 atm

The trend is similar with increasing pressures. In the reduction data at 750 °C, the reactivity of the particles increases with increasing pressure. The conversion times for 1.3 atm, 10 atm, and 20 atm can be seen to decrease with increasing pressure as shown in Figure 17 given below. The 50% conversion time is 5.6 min, 4.9 min, and 4.8 min for 1.3, 10, and 20 atm respectively.

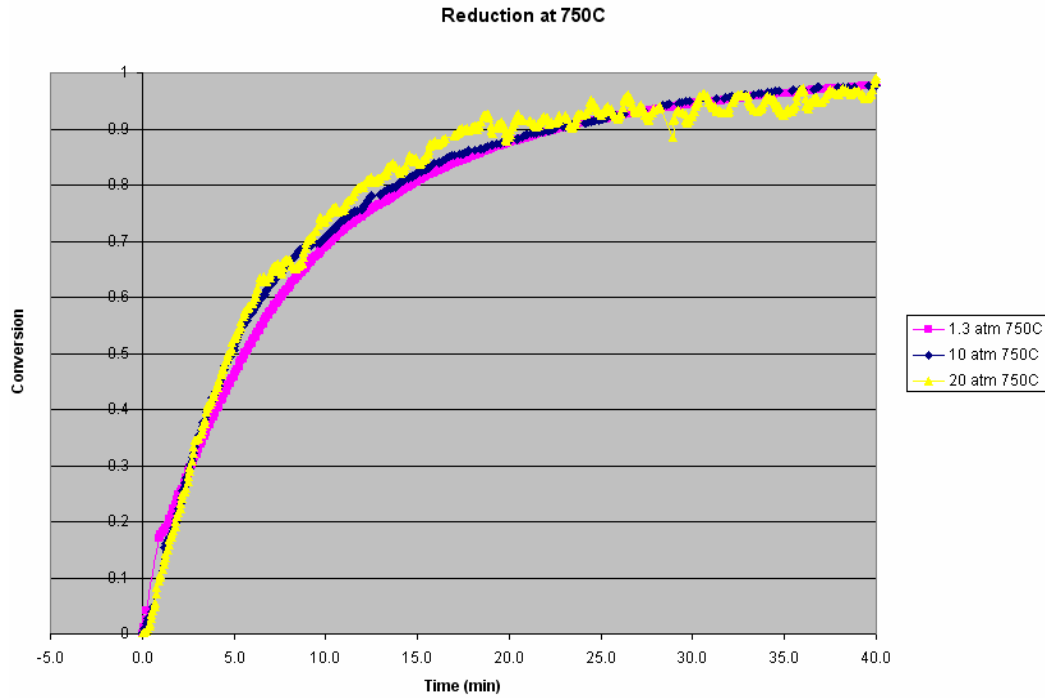


Figure 17: Reduction with hydrogen at 750 C

At 20 atm however, the experimental data is in disagreement with theory when considering only kinetic effects. The reaction curves appear to be superimposed on top of each other meaning that the reactivity of the particles is the same regardless of the temperature. However, this analysis along with the analysis performed by Garcia-Labiano does not consider mass transfer limitations or a laminar flow regime. The assumptions made are that the mass transfer limitations are small compared to kinetic limitations and that the reactant concentration at the surface of the particle is equal to the bulk concentration. The data in Figure 18 shows evidence of a reactant gas boundary layer effect. The possibility of the existence of a gas boundary layer is further confirmed when considering the flow regime present in the TGA.

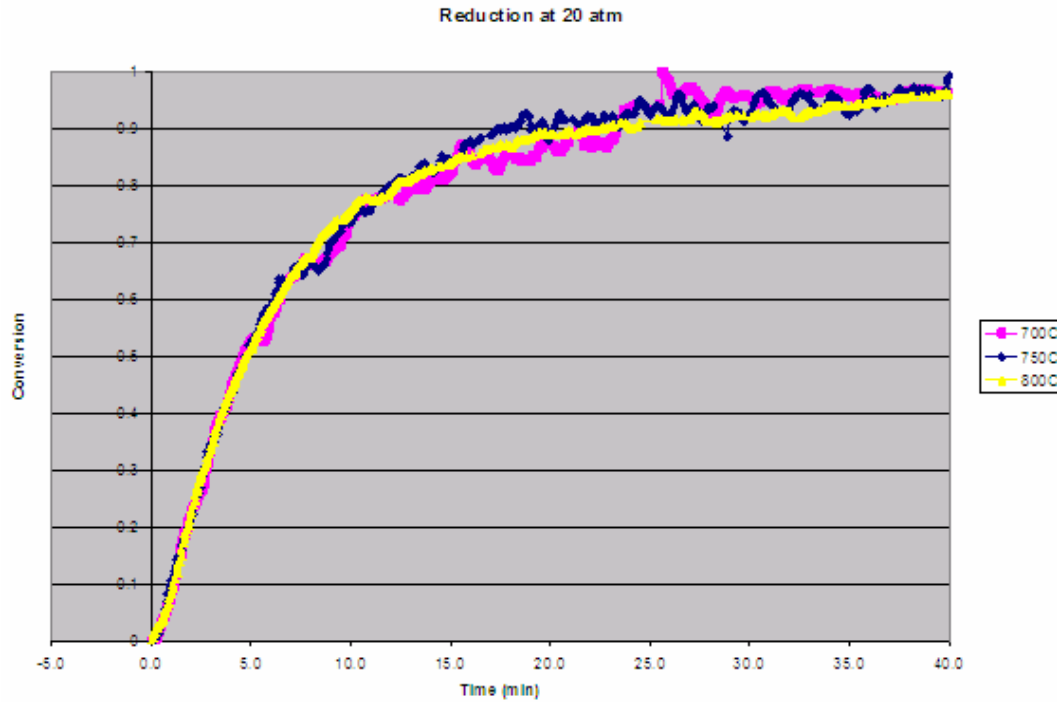


Figure 18: Reduction with hydrogen at 20 atm

In order to determine the flow regime within the TGA, the Reynolds number needs to be considered. Reynolds number can be determined from Equation 3 given below where ρ is the fluid density, V is the superficial fluid velocity, D is the pipe diameter, ν is the kinematic viscosity, and μ is the viscosity.

$$Re = \frac{\rho V D}{\mu} = \frac{V D}{\nu}$$

Equation 3: Reynolds number¹¹

For cylindrical pipes, the transition from laminar to turbulent flow occurs around $Re=2100$ ¹². Before the Reynolds number can be calculated, the mean velocity needs to be determined. At pressures up to 10 atm, the ideal gas law is valid; however, pressures of 20 atm need to be treated using other more complex equations of state. Equations of state are generally used for pure components, but mixing rules are available for accurate

calculations. The Peng-Robinson equation of state is given below in Equation 4 where P is pressure, R is the ideal gas constant, T is temperature, V is molar volume, a(T) and b are constants specific to the molecule of interest.

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)}$$

Equation 4: Peng-Robinson equation of state

In order to apply the equation properly to gas mixtures, the mixing rules, shown in Equation 5, which affect the constants of the Peng-Robinson, must be considered. The binary interaction parameter from Equation 6, k_{ij} , can be assumed to be equal to zero because nitrogen and hydrogen are both diatomic non-polar molecules. This assumption is supported by the thermodynamic data in Sandler which shows that N_2 and CO_2 have an interaction parameter of -0.02 while N_2 and $n-C_6H_{14}$ have an interaction parameter of 0.15¹³.

$$a_{mix} := \sum_{i=1}^C \sum_{j=1}^C (y_i \cdot y_j \cdot a_{ij}) \quad b_{mix} := \sum_{i=1}^C (y_i \cdot b_i)$$

Equation 5: Mixing rules for the Peng-Robinson

$$a_{ij} := \sqrt{a_{ii} \cdot a_{jj}} (1 - k_{ij}) = a_{ji}$$

Equation 6: Combining rule for the Peng-Robinson

Using the equations listed above, the flow rate of gas in the TGA at 750 °C, 20% hydrogen, and 20 atm was calculated to be 0.0729 Lmin⁻¹ which corresponds to a molar volume of 4.247 Lmol⁻¹. For a Reynolds number of 2100, the necessary viscosity of the gas was calculated to be at most 5*10⁻⁶ cP. At room temperature, the viscosity of a gas is approximately 0.001 cP and increases with increasing temperature. The low Reynolds

number confirms the presence of a laminar flow regime causing a boundary layer to form around the sample. The laminar flow regime gives evidence that the reaction at 20 atm is diffusion limited rather than kinetically limited.

The Thiele modulus allows for a comparison between the kinetic rate and the diffusion rate. Equation 7 gives the Thiele modulus. Generally, when ϕ is calculated to be less than 0.3, the system can be considered to be kinetically limited. When ϕ is greater than 20, it can be considered mass transfer limited¹⁴. When comparing the guidelines to the equation for the Thiele modulus, a higher reaction rate would cause the Thiele modulus to increase while a higher diffusivity would cause it to decrease.

$$\phi = \sqrt{\frac{k''' L^2}{D_{AB}}}$$

Equation 7: Thiele modulus

In this case, since the data shows that the reaction at 20 atm is reaction limited, the Thiele modulus would show that the parameters would place the reaction into the diffusion limited zone.

Conclusions and Recommendations

Pelletization

The scaled up process has proven to be effective in producing large amounts of pellets within a reasonable timeframe. With the addition of the granulation step, the pellet production rate has increased from the order of $\sim \text{gday}^{-1}$ to kg hour^{-1} . The pellets have shown reactivities similar to the previously produced pellets from the dry-mixing process. This new method is also cost effective in terms of raw materials used. Beyond the raw iron and support feedstocks, it uses water and corn starch which are both cheap reagents.

The scaled up process is currently limited by the size of the mixing drum. The maximum manageable amount of powder is approximately 2 kg. A larger mixer of a style other than a rotary drum would be preferred. With the drum mixer shown in Figure 5, the larger particles would float to the top of the finer particles. This caused problems with mixing which required human intervention to manually break the agglomerated particles. Larger grinding media greater than $\frac{1}{2}$ " diameter would also help with the breaking of the particles because the $\frac{1}{2}$ " media could not always supply enough force to break the agglomerates.

High Temperature Quartz Studies

The high temperature quartz studies on the particle size and kinetics only investigated low pressures and pure reactants, i.e. CO/H_2 mixtures were not considered. If interactions between reactant mixtures exist then the experimental design for this experiment cannot detect them because there is no data on gas mixtures. Future studies should include gas mixtures in order to simulate the reaction with syngas. Data from

high pressures would also be valuable in to simulate the actual operating conditions of the SCL process.

Effects of Pressure on Reduction Rates

The pressure effect studies were able to show the general trend of reactivity with respect to temperature and pressure. The findings were the opposite of what was reported by Garcia-Labiano. Garcia-Labiano published that increasing pressure caused lower reactivities. There was evidence of boundary layer formations at higher pressures due to lower superficial gas velocities within the TGA, and it is believed that the mass transfer limitation caused by the boundary layer is responsible for their results. The reactivity increases with pressure and temperature.

The experimental set up for the high pressure investigation was limited in that it could not supply sufficient gas velocities to reduce the effect of the boundary conditions. In a real commercial system, the flow rates of gases will be sufficiently high such that there would be a small boundary layer. The small boundary layer would make the kinetic limitation dominant over the mass transfer limitation. To allow for the study of kinetics without the mass transfer effects at higher pressures, higher gas velocities are needed. The high pressure TGA should be retrofitted with mass flow controllers capable of delivering the appropriate amount of gas.

The only reactant used was hydrogen whereas the coal derived syngas, as well as other types of syngas, will contain a mixture of mainly hydrogen and carbon monoxide. Further studies with carbon monoxide and mixtures of carbon monoxide and hydrogen would be valuable for giving kinetic data which would not only be applicable to the SCL system, but also other iron based looping systems.

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